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SOLUBILITY OF XYLITOL, SORBITOL AND MANNITOL IN BINARY LIQUID MIXTURES OF METHANOL AND ETHANOL AT DIFFERENT TEMPERATURES

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Building blocks are molecules with multiple functional groups with the potential to be transformed into new useful molecules, able to be converted in secondary chemicals used as plasticizers, pH control agents, resins, solvents and many other functions. In the interest of obtain these molecules, processes such as hydrolysis and depolymerization are able to break the bigger molecules into small saccharides to be converted into compounds of interest. Considering that, carbohydrates are the most abundant chemicals on planet, sugars and some of their derivatives like sugar alcohols are a prominent alternative to be considered.

According to the U.S. Department of Energy, sorbitol and xylitol are among the most eminent sugar alcohols and have a wide range of applicability not only directly in nutrition, cosmetic and medicine, but also as high potential building blocks. In addition, they have been considered two of the top twelve building blocks with higher potential to yield high-value bio-based chemicals or materials. The obtainment of these building blocks finds some barriers. Higher yields, separation and cost-efficient are some of the drawbacks to be solved. Part of these challenges can be supported with studies of solid-liquid equilibrium.

In order to contribute with the thermodynamic studies of mixtures and processes of separation, this work presents an experimental evaluation of xylitol and sorbitol solubility in methanol-ethanol binary mixtures, for the temperatures of 293.2 K, 303.2 K, 313.2 K, and 323.2 K, and the solubility of mannitol for the temperatures of 313.2 K and 323.2 K.

The determination of solubility in the binary solutions formed by ethanol and methanol was performed by gravimetric method. Each of the solids studied was previously dried in an electrical furnace and kept in a desiccator until use. The binary solutions were previously prepared for each molar fraction and placed in a volumetric flask to be easier homogenized and stored until the beginning of the experiment.The binary solutions and an excess of solid were transferred to a jacketed glass cell, also known as equilibrium cell, connected to a thermostatic bath.

The temperature of the mixture inside the equilibrium cell was monitored using a bulb thermometer, and to ensure the contact of the liquid solution and the solid during the dissolution process, it was used a magnetic stirrer. After feeding the equilibrium cell with the binary mixtures and the excess of solid, it was adjusted the stirring speed and the thermostatic bath temperature, then the circulation system of the heating fluid was activated. The system remained under intense agitation for 3 hours, to guarantee the contact among the components and provide mass transfer.

Concluding the agitation period, the system was kept under no agitation for 5 hours, to certify the solid-liquid phase separation. A sampling system was prepared with a plastic syringe connected to a stainless steel catheter and both connected to the vessel's lid. Aliquots of 10 ml were taken out in triplicates, and placed into flat-bottom flasks of known weights, covered with glass lids. The samples were kept in a desiccator to equalize the temperature and their masses were determined. The glass vessels with the samples were placed into an electrical furnace at 353 K, in order to allow the solvent evaporation. After sampling, a new amount of solid and solution were put into the equilibrium cell and a new temperature was set, to start the experiment again.

The data expressed in mass fraction w_s as a function of molar composition of ethanol x_2 are presented in Figure 1, where in graphics (a), (b) and (c) show the solubility of xylitol, sorbitol and mannitol, respectively. Analyzing the data, it was observed an increase of solubility as the temperature increases for all the solids studied. The process of dissolution may be followed by two steps, first the solid melts becoming a liquid, and second the two liquids are mixed. The process of fusion of the solid is endothermic; hence, a higher temperature increases the solubility.

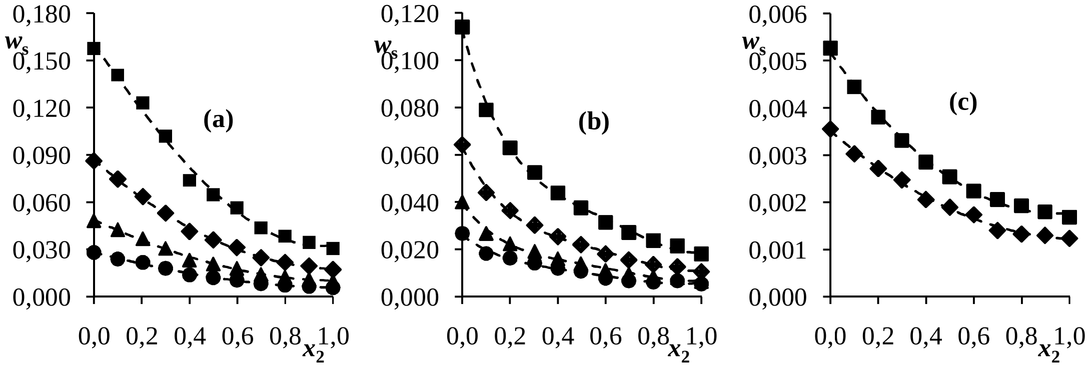

Figure 1. Solubility of xylitol (a) sorbitol (b) and mannitol (c), as function of ethanol's molar fraction in the binary solution: ● 293 K; ▲ 303 K; ♦ 313 K; ■ 323 K.

Xylitol has a highest solubility for each composition of the binary liquid mixture followed by sorbitol and mannitol respectively. The solubility of a component does not depend only on the temperature, but also on the spatial arrangement of the molecule and on the dielectric constant of the binary solution. Xylitol is a linear molecule, composed by five hydroxyl groups, each one bounded to a carbon atom. Sorbitol and mannitol are isomers, composed by six atoms of carbon and six hydroxyl groups. The highest solubility observed for xylitol assay is due to its size, as xylitol molecule is smaller than sorbitol and mannitol, it makes more stable bounds with the components present in the binary mixture. The molecules of mannitol and sorbitol have the same size, but they present a different orientation of the hydroxyl group in the second carbon atom. For this reason, sorbitol has a higher interaction with the components present in the binary mixture, being more soluble. The solubility is also affected by the concentration of the binary liquid mixture.

For all the solids studied, it was observed that the solubility is higher in ethanol than in methanol. It was observed that the addition of ethanol in the mixture leads to a reduction of solubility. All the solids studied in this work are polar molecules, with a higher affinity by methanol, which has a higher dielectric constant than ethanol at the same temperature. The reduction of solubility due to the addition of an anti-solvent is related to the decrease of the dielectric constant of the binary mixture. A mixture of methanol and ethanol leads to the formation of a solution with intermediate dielectric constant reflecting therefore in intermediate values of solubility as is observed. Moreover, the mixture of methanol and ethanol is followed by a contraction of volume (negative excess molar volume) which may influence the attraction force and therefore there is a decrease of solubility.